RESEARCH REPORTS

CHAPTER 1

An Overview of the 1997 NHMFL Research Reports

The year 1997 showed the continued maturation of the laboratory, with the interfaces between the research groups being strengthened. This is particularly true for the interface between the Science program and the Magnet Science and Technology (MS&T) activities in the laboratory. Thus, it is appropriate that the format of this report reflect these ties by combining the MS&T reports with those of the Science program.

This year the total number of reports is 255 as compared to 193 and 239 in the previous two years. Most important, however, is the increasing quality of the research as is evident from the individual reports. To highlight a few key discoveries in the past year we present an example from the various areas of research in the laboratory. As the reader will see, we could have chosen many other examples of equal importance.

Biology. Because of the diversity of its applications, magnetic resonance is having a tremendous impact on the study of biology. Using the same technological approaches, magnetic resonance can study a range of biological systems from molecules to humans. The application of magnetic resonance to the study of biology is creating a revolution, which is well illustrated by the breadth of the research reported here.

In the NHMFL, molecular studies have been carried out on muscle contraction, the structure of metal-containing proteins, and electron transfer in photosynthesis using electron magnetic resonance spectroscopy. Using ion cyclotron resonance, protein molecular mass has been resolved to a level of a single proton thus allowing characterization of structure and dynamics in large protein molecules. Nuclear magnetic resonance spectroscopy has been used to study the structure and function of channel-forming proteins, neuropeptides active in the cytoplasm, and neuropeptide precursor proteins.

Also in the NHMFL, the same magnetic resonance technology has been used to study intact tissue. Specifically nuclear magnetic resonance imaging has been used to study ischemia in perfused brain, measure electric current in excised nervous tissue, and visualize the functioning brain of humans. In addition, the motion of water and important metabolites in tissue has been measured using nuclear magnetic resonance yielding new information about molecular dynamics within intact tissue.

These studies represent the broad range of current scientific studies in biology currently underway at the NHMFL. As higher field magnets become available, the methodology for and applications of magnetic resonance to the study of biology will continue to grow and provide new information, so that magnetic resonance will continue to be a premier tool in biology.

Chemistry. The drug industry is moving explosively into the synthesis of “combinatorial” libraries of molecules, because such techniques make it possible to make a x b x c (e.g., 10^4 to 10^6) different drugs in a + b + c (e.g., 20 to 100), robotically conducted reaction steps, in which a, b, and c are the numbers of different possible substituents at each of three positions on the molecular frame. It is still necessary, however, to screen the full library to see which drugs bind to the biological receptor of interest. In 1997, NHMFL researchers at University of Florida used the 9.4 T FT-ICR mass spectrometer in Tallahassee to resolve and identify individual members of various combinatorial libraries, both before and after binding (non-covalently) to a receptor. That approach should make possible the simultaneous evaluation of large numbers of strongly-bound (and thus highly effective) drugs in a single step. See Eyler, *et al.*, p. 27.

Geochemistry. In the field of isotope geochemistry, the decay of naturally occurring radioactive nuclides has been used to study the differentiation and evolution of the Earth, and its oceans and atmosphere, as well as the origin and history of our sun and solar system. In fact, the abundances of long-lived radionuclides in our solar system have provided crucial clues as to the age of the universe itself. As the discipline of isotope geochemistry in the study of the Earth has matured over the past three decades, more and more parent-daughter systems have been exploited as the technology to measure ever-smaller differences between isotope ratios, and ever-smaller quantities of material, has been developed. The uranium and thorium decay series have played extremely important roles because the nuclides that comprise these systems have half-lives that are appropriate for the study of processes that occur over time spans ranging from days to gigayears. Among the more important components of these series is the decay of ^{238}U, with a half-life of 4.5×10^9 years, to ^{230}Th, with a half-life of 75,000 years. The in-growth or decay of ^{230}Th can be used to study recent volcanism, in terms of volcanic processes and hazards, as well as changes in the Earth's climate over the past several hundred thousand years. Until recently, the relatively low abundance of ^{230}Th compared to long-lived ^{232}Th (on the order of one part in 2×10^5 in most materials) necessitated its measurement by alpha-decay counting techniques, with comparatively large sample requirements and ultimate precisions limited to about 2% (at the 2σ confidence level). By counting atoms instead of decays, using a unique sputter-source, magnetic-sector mass spectrometer optimized for high-precision isotope ratio measurement at the NHMFL, improvements in both sample size and measurement precision on the order of a factor of twenty have been realized over alpha-counting and conventional thermal ionization techniques. These technological advances have enabled us to address problems concerning the chemical evolution and differentiation of the Earth, through studies of young volcanic rocks in a variety of tectonic environments including mid-ocean ridges, ocean islands, and island arcs, which could not previously be addressed in a practical manner. See Zindler, *et al.*, p.39.

Superconductivity–Basic. A key issue in understanding of superconductivity of the cuprates is the existence of a decrease of the spin susceptibility with decreasing temperature even at temperatures above T_c It has been suggested that this effect is due to pairing fluctuations above T_c that lead to a pseudogap for spin excitations. Hammel, *et al.*, (p. 48) have carried out NMR measurements of the susceptibility in strong magnetic fields to understand this effect. They find that the spin gap behavior is suppressed by the magnetic field, lowering the temperature below which spin pseudogap behavior is observed. This result is consistent with the interpretation that the pseudogap arises from pairing fluctuations in the normal phase, corresponding to short range pairing order in the absence of long range order that produces the Meissner effect.

Superconductivity–Applied. Although many challenges must be overcome for the successful development of high temperature superconductor (HTS)-based superconducting magnets (SCMs), the primary obstacle is the critical current density (J_c) as a function of temperature, magnetic field, and mechanical state. Ultimately, the size, cost, and feasibility of any SCM is driven by the conductor J_c. A variety of factors, intrinsic and extrinsic, play a role in determining J_c of a material. NHMFL research includes methods to improve the intrinsic intragranular J_c via flux pinning and characterization of conductors under a variety of magnet-relevant conditions for both a fundamental understanding and engineering database development. For a superconductor to have a large intergranular J_c, it must first have an even larger intragranular J_c. In HTS materials at high fields or elevated temperature, the intragranular J_c is limited by weak flux pinning. In the research reports by Schwartz, *et al.*, (pp. 72, 73), NHMFL researchers report on two effective additives that significantly improve the flux pinning in $Bi_2Sr_2CaCu_2O_x$ (Bi2212). One approach, using non-reactive nanoscale MgO additions, directly adds pinning centers into the Bi2212 grains. The other approach, using BaO_2 additions, precipitates pinning centers via the Ba-based phases that grow during the heat treatment. Thus, these two approaches compare the effectiveness of reactive and non-reactive additions. NHMFL researchers also report on the effects of mechanical stress and strain on J_c. Understanding this behavior is essential for the development of SCMs because the transport J_c must be maintained despite the presence of large tensile stresses resulting from the Lorentz forces. Furthermore, understanding how stress and strain effect the transport critical density assist in understanding the fundamental nature of intergranular transport and the role of microcracks upon it. These two topics, which represent only a small fraction of NHMFL research on HTS materials, illustrate the underlying scientific approach of the program, which is to improve HTS materials for engineering applications by better understanding their inherent physical behavior.

Quantum Fluids. One of the most important challenges in low temperature physics and in spin systems polarized in high magnetic fields and low temperatures is identifying mechanisms to transport heat and magnetization across interfaces. These studies show for the first time that quantum mechanical zero point motions can do this at metal to liquid ^{3}He boundaries, in analogy with previous studies (Kuhns, *et al.*) on insulators. See Sullivan, *et al.*, p. 77.

Although the ordering of quantum rotors has been studied in three dimension, their studies of the nature of the ordering in two dimension was particularly significant as it demonstrated the effect of enhanced quantum correlations on the nature of the transition to ordered states in geometrically frustrated (quantum rotor) spin-1 systems. See Sullivan, *et al.*, p. 77.

Kondo/Heavy Fermion Systems. The physics of Kondo insulators remains mysterious. In the case of SmB_6, researchers have found that the dilute Sm ion in a semimetallic hexaboride lattice is compensated by its own extra outer electron, forming a kind of local Kondo singlet, indicating the possibility to describe Kondo insulators as arising from a set of such local singlets.

In dense Kondo lattices, moment-moment interactions have never been effectively isolated experimentally. Surprisingly, de Haas-van Alphen experiments in the series $La_{1-x}Ce_xB_6$ have been possible, so far out to x = .6. These offer good hope that these interactions can be quantitatively determined in this system and for the first time. See Fisk, *et al.*, p. 80.

Molecular Conductors. Three leading challenges face the physics of low dimensional (molecular) conductors:

- What microscopic mechanisms (spin, orbital) accompany the behavior of low dimensional ground states?
- How does the Landau level spectrum behave in the near quantum limit?
- Can high fields sort out some of the details of Fermiology?

The answers to these questions truly need very high, indeed the highest, magnetic fields to explore the details of the low dimensional physics that they manifest. The experimental challenges have been to carry out accurate resonance, Hall, and magnetization studies in very high magnetic fields to determine microscopic, quantum, and thermodynamic parameters associated with various novel low dimensional ground state properties. And indeed, in the last year, on a number of fronts, significant progress has been achieved.

With respect to the first question, in the area of nuclear resonance, notable developments include proton and ^{13}C studies above 20 T that are probing the microscopic details of spin density and conduction electron mechanisms in low dimensional ground states. What is most impressive is that these very high field NMR studies are probing, with increasing accuracy, spin-lattice, spin-spin, and Knight shift effects. Through their temperature and field dependence, the processes that drive them are emerging. Also of note is the area of electronic resonance where progress has been made with resonant cavity methods up to 30 T to determine the anisotropy of the complex conductivity in a number of materials with different ground state configurations. See Brown, *et al*, p. 97; Clark, *et al*., p. 98; Kuhns, *et al*., p. 108; Hill, *et al*. p. 104.

As for the second question, recent Hall effect measurements are giving a strong indication for quantum Hall behavior at low Landau level index in a quasi-two dimensional metal. This work has stimulated both discussion and further investigations into "chiral" behavior and novel current paths in these otherwise bulk, layered, really quasi-three dimensional materials. This work is quite novel in that the proposed pinning mechanism involves open orbit bands that coexist with those with the Landau level spectrum. Of note is the application of uniaxial stress to alter the nature of this pinning mechanism. See Harrison, *et al*., p. 103; Honold, *et al*., p.108; Brooks, *et al*., p. 94.

The third question has an easy answer: yes. In two cases, pulsed magnetic fields have solved long standing problems. First, as one would expect from simple band structure calculations, quantum oscillations should be observed in a high temperature (12 K) organic superconductor, and indeed they are. This puts an end to speculation about very heavy electron masses, or anomalously large scattering rates that arise because of the high T_c character. The other question involves a magnetic breakdown orbit in another material, which some assigned to a Fermi surface reconstruction. Its observation in the high field metallic state ensures that it arises from the underlying normal state Fermi surface topology. See Honold, *et al*., p. 106; Mielke, *et al*., p. 110.

In this section the reader will find many more excellent investigations of these materials, almost exclusively carried out in high magnetic fields, and in one case up to 145 T.

Semiconductors. Haetty, *et al*., (p.118) have carried out a study of superlattice samples that exhibit photoluminescence (PL) due to recombination of electrons in the AlAs with holes in the $Al_{0.25}Ga_{0.75}As$. The PL intensity is controlled by the wave function overlap of the electrons and holes. When the magnetic field is parallel to the interfaces, it has no effect on the PL, but when it is perpendicular to the interfaces, the PL intensity drops off as the magnetic field is turned on. This indicates that the magnetic field is localizing the electrons and holes at different points in the planes of the interfaces. This work is an excellent example of how application of strong magnetic fields can help understand optical processes in semiconductors.

Magnetism and Magnetic Materials. The development of spectroscopy in the 35 to 200 GHz range that physicists term "the missing frequency gap," because of the lack of available instrumentation, are of paramount importance in many fields of solid state physics. Such developments will allow for the study of cyclotron resonance, conductivity in the millimeter wave area in an energy range of interest to probe elementary excitations. The NHMFL developed a cavity based spectrometer continuously tunable from 35 up to 115 GHz. Application to Mn_{12} spin cluster demonstrates the potential of the technique and brings information, not otherwise available, regarding the energy levels immediately below the top of the barrier that may be crucial to the magnetization relaxation mechanism of this system.

Such studies bring new insight in the quantum tunnelling of magnetization in nanomagnets. See Hill, *et al.*, p.146.

One of the leading challenges in the field of photosynthesis is the determination of the electronic structure of the components involved in oxygenic photosynthesis, because electron transfer is the fundamental mechanism of photosynthesis. Such a determination can be achieved through the measurement of the g-Lande tensor components. Using high-field/high-frequency EPR at and above 11 T/330 GHz, the g-factor anisotropy of the primary donor radical cation P700+ has been resolved in plant photosystem I from a powder spectrum. The g-anisotropy was measured in a temperature range from 5 to 260 K. This is the first time a non-deuterated chlorophyll radical cation EPR spectrum has been resolved. Such results provide the basis for electronic structure models of the primary electron donor of photosynthesis. See Bratt, *et al*., p. 8.

Other Condensed Matter. Magnetic field induced changes in electronic transport can often reflect unusual and novel behavior in condensed matter systems. Sometimes the results are unexpected as is the case for two of the research activities reported here. In the first (Cornelius, *et al*., p. 163) measurements of the de Haas-van Alphen (dHvA) oscillations in the magnetization of the antiferromagnet UGa_3 in fields up to 50 T have uncovered an unexpected reconstruction of the Fermi surface that correlates with a magnetic transition observed at 13 T. Although similar techniques have been used in previous studies, these new results show that careful analysis of the commensurabilities of the frequency spectrum of dHvA oscillations above and below a suspected magnetic transition can confirm a concomitant change in electronic structure. In a second report (Hebard and Aranson, p.164), measurements of the magnetoresistance of silver films prepared in the coalescence regime reveal a classical magnetoresistive behavior having a quadratic field dependence but with an unexpected negative sign. This behavior arises because transport is dominated by electron flow in narrow twisting channels. The work suggests that some exotic "bad" metals, which exhibit metallic behavior on anomalously high resistivity scales, are in fact quite normal "good" metals when extreme geometrical corrections in the determination of resistivity are taken into account.

Magnetic Resonance Techniques. Over the past 20 years or so, high-resolution NMR spectroscopy of molecules in liquid solution has been revolutionized by a host of two-dimensional Fourier transform techniques (COSY, NOESY, etc.). Such methods are typically based on spin correlations arising from scalar (through bonds) or dipolar (through space) couplings. In 1997, NHMFL NMR researchers conceived and demonstrated a new type of two-dimensional experiment for solid samples, in which the second dimension is created by a temperature-jump, so that off-diagonal peaks in the two-dimensional spectrum reveal the connections between nuclear spins at two temperatures (e.g., before and after "melting"). The method is made possible by the very long spin-lattice relaxation time, T1, in solids, so that magnetization can be preserved for several minutes to allow for attainment of a new equilibrium following a temperature-jump. The inventors of this technique used its enhanced resolution to sort out various possible proton exchange mechanisms in solid squaric acid. See Fu, *et al*., p. 171.

In addition, in 1997, the NHMFL ICR group introduced a new technique that promises to extend by an order of magnitude the largest protein that can be usefully analyzed by mass spectrometry. Using isotope-enrichment techniques well-known in NMR, the authors depleted (rather than enriched) proteins in carbon-13 and nitrogen-15, to yield a narrower and stronger isotopic mass distributions. Specifically, the "monoisotopic" species (i.e., molecules in which all carbons are carbon-12, all nitrogens are N-14, etc.) becomes directly detectable for unambiguous determination of protein molecular weight to within 1 Dalton. The method becomes especially powerful in combination with H/D exchange (to identify surface-accessible backbone amide protons in proteins). Applications now under way include studies of protein folding mechanisms, protein conformational change on binding of drugs/ inhibitors, mapping of protein:protein contact surfaces for systems too large or intractable for NMR or x-ray diffraction, and identification and quantitation of the "proteome" (i.e., all of the proteins in a given organism or tissue type) without conventional two-dimensional gel electrophoresis. See Senko, *et al*., p.186.

Engineering Materials and *Magnet Technology*. In order to make an accurate magnet design, and to have knowledge of the performance and margins in a design, it is essential to know the relevant properties of the component materials. This is all the more important as the performance of the device becomes more demanding. The 900 MHz magnet contains both unique materials, and materials being used in extreme conditions. In order to support the design of the magnet, measurements are made of relevant materials properties. Examples in the reports include the reinforcement and the NbTi conductor. Although the reinforcement is expected to have sufficient strength, it experiences a high temperature heat treatment. There is a question as to the residual strength after the partial anneal. The NbTi conductor must have adequate n-value for persistence. In the 900 MHz magnet, the NbTi conductor is used at high field and reduced temperature, and the resulting n-value is given by the reported measurements. See Dixon, *et al*., p. 194 and p. 195.

Cryogenics. Cryogenics is an applied field of low temperature physics and engineering. We pursue many research and development activities based on requirements of the application rather than being motivated by basic understanding. The four research reports are best placed in this context. For further clarification, I will focus on the two reports involving He II cryogenics. The paper by Welton, *et al*., (p. 218) involved heat transport in He II contained in a channel immersed in a constant temperature He II bath. This is an idealized geometry for a He II heat exchanger such as in the 45-T Hybrid, for which there is no clearly defined theory of design. The principal issues are to determine the thermal profile in the channel using the known transport properties of He II. In addition, it is of interest to investigate cavitation phenomena that might occur due to the local temperature exceeding the saturation temperature. These limits were studied analytically and compared to an experiment. The agreement indicates that the theoretical basis for design of He II heat exchangers is established.

In the paper by Panek, *et al*., (p. 217) a similar issue of He II heat transport applied to application was studied. In this case, the goal was to control He II level in two separate reservoirs, which are at different temperature but connected by means of liquid and vapor channels. The idea was to use the thermomechanical effect through a porous plug to provide compensation for the vapor pressure difference. Analysis shows that such a balance can be achieved using a channel with pore size of order 10 microns. The data in Figure 2 of this report confirm that equal levels can be achieved for finite heater power, in this case for a pore size of order 30 microns. This result may allow large scale He II systems to be designed with passive level control devices installed.

The above reports give an impression of some of the exciting work at the NHMFL. The close coupling of the external users and the in-house research staff is evident from the reports. As in previous years these studies have implications for advanced technology as well as advancing the forefront of science over a broad range of disciplines.